Theoretical developments and computational studies in chiroptical spectroscopies

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Thesis Statements

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Introduction

Recent successes in optical resolution of chiral fullerenes and single-walled carbon nanotubes (SWCNT) have increased the interest in chiroptical characterization of chiral carbon nanostructures (CCNS). So far only electronical optical activity has been measured for CCNS samples. We study vibrational Raman optical activity (ROA), i.e. optically active inelastic light scattering accompanied by vibrational transitions. Preceding forthcoming experiments we present the first theoretical Raman optical activity (ROA) spectra of chiral fullerenes and SWCNT.

High complexity of chiroptical spectra necessitates quantum chemical modeling for interpretation and assignation. Two main steps of ROA simulation are the calculation of spectral line positions and intensities. We obtained harmonic vibrational frequencies and normal modes by density functional theory (DFT) using standard program packages. Implementations are available for ROA as well, utilizing the so-called far from resonance (FFR) approximation. The FFR approximation is valid, when the frequency of the incident light (ω) is small compared to the energy of the electronic transitions. The ROA intensity in the FFR model is expressed with the derivatives of three polarizability tensors ($\tau_{\alpha\beta}$) with respect to the normal coordinates. Using a common notation for all three polarizability tensors, their expressions read:

$$\tau_{\alpha\beta} = \sum_{e_j \neq e_0} \left[\frac{\langle e_0|\hat{d}_\alpha|e_j\rangle\langle e_j|\hat{V}_\beta|e_0\rangle}{\omega_{e_j e_0} - \omega} + \frac{\langle e_0|\hat{V}_\beta|e_j\rangle\langle e_j|\hat{d}_\alpha|e_0\rangle}{\omega_{e_j e_0} + \omega} \right], \tag{1}$$

where $\hat{V}_\beta$ is a general multipole operator, which could be the electric dipole ($\hat{d}_\beta$), magnetic dipole ($\hat{m}_\beta$) and the electric quadrupole ($\hat{\Theta}_{\beta\gamma}$) in case of the three different polarizabilities. Furthermore, $|e_0\rangle$ is the ground electronic state, while $|e_j\rangle$ denotes the wavefunction of the excited states and $(\hbar)\omega_{e_j e_0} = E_j - E_0$ is the energy difference between these states.

State of the art ab initio implementations for ROA intensities can not be applied for systems accommodating hundreds of carbon atoms. For this reason, cost-effective, one-particle π-electron methods were developed to compute spectral intensities of CCNS

systems. When computing ROA spectra (and comparing the π-electron models with references), equilibrium structure and normal coordinates are obtained with DFT methods and polarizability derivatives are computed at the π-electron level.

In the simplest Hückel type model only first neighbour interactions are considered. The Hückel parameters depend on the coordinates of the nuclei, hence differentiation with respect to the normal coordinates can be carried out. Due to the limitations of the first neighbour parametrization, the Hückel model can not be applied for conjugated systems with high curvature.

In order to improve on ROA intensities, a generalized π-model (all-π) is introduced in which parameters describing interaction between all atoms are derived in a system-specific manner. The all-π method is based on an effective π-model introduced in our laboratory (Phys. Rev. B, 77:103407, 2008). Improvements are made in the parametrization procedure (using Hartree–Fock (HF) instead of semi-empirical) and the overlap of the atomic orbitals are taken into account.

If the frequency of the incident light is comparable to the electronic transitions of the system – like in case of CCNS and $\omega = 532$ nm – resonance occurs. In case of resonance, the first term in Eq.(1) is not meaningful, because $\omega_{e_j e_0} - \omega$ in the denominator tends to zero. Resonance is taken into account in our computations using the short time approximation (STA), in which the relaxation from an excited state of the interacting system is considered fast compared to the time scale of the vibrational motion. STA polarizabilities are similar to the FFR polarizabilities in Eq.(1). There is one important difference, namely, that the STA denominators, $\omega_{e_j e_0} \pm \omega \pm i\Gamma$ are meaningful in case of resonance as well.

FFR and STA ROA spectra of fullerenes are computed using both the Hückel and the all-π method. In case of SWCNT, their translational and occasionally helical symmetry is exploited. For periodic systems, multipole operators describing light-matter interaction have to exhibit periodic symmetry, which is not fulfilled for the conventional multipole operators. Additionally, states of periodic system are described by complex wavefunction, which has to be taken into account in the polarizability formulae.

Normal coordinates of SWCNT were constructed in cooperation with László Biró utilizing the Hessian matrices computed by János Koltai. The most intense bands in the first order Raman spectrum of SWCNT correspond to the radial breathing mode (RBM) and the G^- and G^+ modes. The G^- and G^+ modes are not characteristic to the nanotubes, while the frequency of the RBM is related only to the diameter. Thus it is complicated to distinguish two SWCNT with similar diameters based on their Raman spectrum. There are other (2-3 orders of magnitude less intense) bands in the experimental Raman spectra, corresponding the so-called intermediate frequency modes. These are more characteristic to a single SWCNT, but much less is known about them in the literature.

Results, thesis statements

I. Theoretical ROA spectra with π-electron models [1]

T1: ROA intensities are derived and implemented using both the Hückel and the all-π model. In case of Hückel, multipole moments and their geometric derivatives are evaluated using the zero differential overlap (ZDO) approximation. For testing purposes, polarizability derivatives are derived and implemented using both time-dependent perturbation theory and liner response theory. The all-π polarizability derivatives are obtained via numerical geometric differentiation using multipole integrals evaluated with STO-6G basis functions.

T2: In order to assess the accuracy of the π-models, to most accurate DFT ROA spectra accessible to us were computed as reference for C_{28}, C_{76} and C_{84}, using far from resonance laser frequencies of 1064 nm and 4256 nm. Polarizability derivatives were computed with the B3LYP density functional employing the aug(sp)-cc-pVDZ basis set for C_{28} and 3-21G+ for C_{76} and C_{84}. Equilibrium structures and normal coordinates were obtained using B3LYP/cc-pVTZ for C_{28} and B3LYP/6-31G* for C_{76} and C_{84}. Raman spectra of C_{76} and C_{84} computed with the B3LYP/6-31G*//B3LYP/3-21G+

method compares well with measurements from the literature.

Comparison of the π-models with the reference revealed, that the Hückel and DFT Raman spectra agrees very well for fullerenes with low curvature (C_{76} and C_{84}). The Hückel ROA spectra compares to the reference worse and can only be applied for enantiomer identification in case of systems with low curvature. We found, that the all-π ROA spectra recovers the HF with more than 90% spectral overlap and provides balanced description for fullerenes with both low and high curvature compared to the DFT reference.

II. Theoretical ROA spectra for periodic systems [2]

T3: Hückel ROA intensities are derived and implemented for semiconductor SWCNT utilizing their translational symmetry. Based on the well known formula for the periodic electric dipole moment, formulae for periodic magnetic dipole and electric quadrupole moments are introduced. It has been shown, that the form of this periodic magnetic dipole operator is in accord with the formulae of the modern theory of magnetization. Polarizability derivatives are obtained only for the 26 Raman active modes using numerical geometric differentiation. For testing purposes, helical symmetry is also utilized and the electric dipole polarizability is derived and implemented via analytical differentiation.

T4: It has been demonstrated, that the antisymmetric combinations of the electric dipole-electric quadrupole polarizability are also involved in the FFR and STA ROA intensity formulae for periodic semiconductors. Since these terms do not contribute to the (FFR/STA) ROA formulae in case of finite systems, it is recommended to study the ROA spectra of periodic systems for the first observation of the antisymmetric combinations.

III. Theoretical ROA spectra of fullerenes and SWCNT [1,2]

T5: ROA spectra of C_{76} and C_{84} fullerenes are presented using experimentally relevant, resonance conditions, in order to assist enantiomer identification in prospective experiments. For that B3LYP/6-31G* normal modes were combined with all-π resonance polarizability derivatives. We found, that the spectral overlap of the all-π spectra computed with 532 nm and 1064 nm is over 0.99, thus the all-π spectra hardly depend on ω. The overlap of the all-π with B3LYP/3-21G+ at 1064 nm is 0.7 for C_{76} and 0.27 for C_{84}, the latter being smaller due to differences only in three 30-40 cm^{-1} wide range of the spectra. Based on that, the all-π resonance ROA spectra is found to applicable for enantiomer identification.

T6: Resonance ROA of six different SWCNT is presented at 532 nm computed with the Hückel method. The signs and intensities of the RBM, G^- and G^+ modes vary significantly in these nanotubes, thus the bands of SWCNT with similar diameter does not necessarily overlap in contrast to the case of Raman spectra. The intensity corresponding to the IFM compared to others are bigger in the ROA than in the Raman spectra. Since the ROA spectra is richer in bands and contains additional information in the signs of the bands, it might be more suitable for SWCNT characterization. Changing the frequency of the incident light the signs of the ROA spectra flips, when ω goes through the first excitation energy, as it is illustrated on the example of the (6,5) tube. This phenomenon could be applied to distinguish overlapping bands of different tubes in a mixture sample.

T7: The intensity maxima of the above CCNS ROA spectra are compared to intensity maxima of small, routinely measurable organic molecules and found to be 3-4 and 5-6 orders of magnitude stronger for fullerenes and SWCNT, respectively. This is promising from the perspective of the measurements investigating CCNS samples with small enantiomeric excesses.

Publications

[1] P. R. Nagy, P. R. Surján, Á. Szabados. Vibrational optical activity of chiral carbon nanoclusters treated by a generalized π-electron method. *J. Chem. Phys.*, 140: 044112, 2014.

[2] P. R. Nagy, L. Biró, J. Koltai, P. R. Surján, Á. Szabados, J. Kürti. Theoretical vibrational optical activity of chiral carbon nanoparticles: Fullerenes and carbon nanotubes. *Phys. Status Solidi (b)*, 251:2451–2456, 2014.

[3] Á. Szabados, P. Nagy. Spin component scaling in multiconfiguration perturbation theory. *J. Phys. Chem. A*, 115:523, 2011.

[4] G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, A. T. Rokob, P. Király, G. Tárkányi, T. Soós. Catalytic hydrogenation with frustrated Lewis pairs: Selectivity achieved by size-exclusion design of Lewis acids. *Chem. Eur. J.*, 18:574–585, 2012.

[5] P. R. Nagy, P. R. Surján, Á. Szabados. Mayer's orthogonalization: relation to the Gram-Schmidt and Löwdin's symmetrical scheme. *Theor. Chem. Acc.*, 132:1109, 2012.

[6] P. R. Nagy, Á. Szabados. Unitary perturbation theory applied to multiconfigurational reference functions. *Int. J. Quantum Chem.*, 113:230–238, 2013.

[7] P. Jeszenszki, P. R. Nagy, T. Zoboki, Á. Szabados, P. R. Surján. Perspectives of APSG-based multireference perturbation theories. *Int. J. Quantum Chem.*, 114: 1048–1052, 2014.

[8] V. Murg, F. Verstraete, R. Schneider, P. R. Nagy, Ö. Legeza. Tree tensor network state with variable tensor order: an efficient multireference method for strongly correlated systems. *J. Chem. Theor. Comp.*, 2015. doi: 10.1021/ct501187j.